



CERTIFICATION

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Tokyo 105-0001, Japan, hereby certify that the following is a true and  
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Patent Application No. 203088/2000 on 30th June 2000.

Place      Tokyo

Date      June 18, 2008

  
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PATENT OFFICE  
JAPANESE GOVERNMENT

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Date of application : 30th June 2000

Application Number : Patent Application No. 203088/2000

Applicant(s) : MITSUI CHEMICALS, INC.

15th June 2001  
Commissioner, Kozo OIKAWA  
Patent Office (Seal)

【Designation of the Document】 Patent Application

【Docket Number】 C02150

【Date of Filing】 30 June 2000

【Addressee】 The Commissioner  
of the Patent Office

【International Classification of Patent】 B32B 27/32

【Title of the Invention】 FOAMED LAMINATE BASED ON OLEFIN

【Number of Claims】 13

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**【Notes for Application Fee】**

**【Preliminary Payment**

**Register Number】**

004477

**【Amount of Payment】**

21000

**【List of Submitted**

**Materials】**

**【Name of Material】**

Specification

1

**【Name of Material】**

Drawing

1

**【Name of Material】**

Abstract

1

**【Number of General**

**Power of Attorney】**

9706391

**【Demand of Proof】**

Demanded

【 DESIGNATION OF THE DOCUMENT 】 SPECIFICATION  
【 TITLE OF THE INVENTION 】 FOAMED LAMINATE  
BASED ON OLEFIN  
【 PATENT CLAIMS 】

【 CLAIM 1 】 A foamed laminate based on olefin  
in which

a substrate layer, consisting of a foamed body ( $X_2$ ) of  
a foamable ethylenic thermoplastic elastomer  
composition ( $X_1$ ) comprising the ethylenic thermoplastic  
elastomer (A) and the foaming agent (B), said ethylenic  
thermoplastic elastomer (A) comprising 5 - 60 parts by  
weight of a polyethylene resin (a-1) and 40 - 95 parts by  
weight of a copolymer based on ethylene/ $\alpha$ -olefin (a-2),  
with the said constituents (a-1) and (a-2) summing up to  
100 parts by weight, and

a skin layer made of an ultrahigh molecular weight  
polyolefin resin (Y)

are laminated,

wherein the said copolymer based on  
ethylene/ $\alpha$ -olefin (a-2) is a copolymer of ethylene, an  
 $\alpha$ -olefin and, optionally incorporated, non-conjugated  
polyene and has a Mooney viscosity  $ML_{1+4}(100\text{ }^\circ\text{C})$  of 90  
- 250 and an ethylene content of 70 - 95 mole % and

wherein the said ultrahigh molecular weight  
polyolefin resin (Y) is one which has an intrinsic  
viscosity ( $\eta$ ) of 3.5 - 8.3 dl/g as determined in decalin  
at 135  $^\circ\text{C}$ .

【 CLAIM 2 】 A foamed laminate based on olefin  
in which

a substrate layer, consisting of a foamed body ( $X_2$ ) of

a foamable ethylenic thermoplastic elastomer composition ( $X_1$ ) comprising the ethylenic thermoplastic elastomer (A) and the foaming agent (B), said ethylenic thermoplastic elastomer (A) comprising 5 - 60 parts by weight of a polyethylene resin (a-1) and 40 - 95 parts by weight of a copolymer based on ethylene/ $\alpha$ -olefin (a-2), with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, and

a skin layer made of an olefinic thermoplastic elastomer composition ( $Z_1$ )

are laminated,

wherein the said copolymer based on ethylene/ $\alpha$ -olefin (a-2) is a copolymer of ethylene, an  $\alpha$ -olefin and, optionally incorporated, non-conjugated polyene and has a Mooney viscosity  $ML_{1+4}(100\text{ }^\circ\text{C})$  of 90 - 250 and an ethylene content of 70 - 95 mole % and

wherein the said olefinic thermoplastic elastomer composition ( $Z_1$ ) is one which comprises, per 100 parts by weight of an olefinic thermoplastic elastomer (C), at least one kind selected from the group consisting of 0.5 - 25 parts by weight of an organopolysiloxane (D), 0.5 - 10 parts by weight of a fluorine-containing polymer (E) and 0.5 - 10 parts by weight of an antistatic agent (F), each in a proportion as given above.

**【 CLAIM 3 】** A foamed laminate based on olefin in which

a substrate layer, consisting of a foamed body ( $X_2$ ) of a foamable ethylenic thermoplastic elastomer composition ( $X_1$ ) comprising the ethylenic thermoplastic elastomer (A) and the foaming agent (B), said ethylenic

thermoplastic elastomer (A) comprising 5 - 60 parts by weight of a polyethylene resin (a-1) and 40 - 95 parts by weight of a copolymer based on ethylene/ $\alpha$ -olefin (a-2), with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, and

a skin layer made of an olefinic thermoplastic elastomer composition ( $Z_2$ )

are laminated,

wherein the said copolymer based on ethylene/ $\alpha$ -olefin (a-2) is a copolymer of ethylene, an  $\alpha$ -olefin and, optionally incorporated, non-conjugated polyene and has a Mooney viscosity  $ML_{1+4}(100\text{ }^{\circ}\text{C})$  of 90 - 250 and an ethylene content of 70 - 95 mole % and

wherein the said olefinic thermoplastic elastomer composition ( $Z_2$ ) is one which comprises, per 100 parts by weight of an olefinic thermoplastic elastomer (C), a polyolefin resin (G) in an amount of 5 - 200 parts by weight.

**【 CLAIM 4 】** A foamed laminate based on olefin in which

a substrate layer, consisting of a foamed body ( $X_2$ ) of a foamable ethylenic thermoplastic elastomer composition ( $X_1$ ) comprising the ethylenic thermoplastic elastomer (A) and the foaming agent (B), said ethylenic thermoplastic elastomer (A) comprising 5 - 60 parts by weight of a polyethylene resin (a-1) and 40 - 95 parts by weight of a copolymer based on ethylene/ $\alpha$ -olefin (a-2), with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, and

a skin layer made of an olefinic thermoplastic

elastomer composition ( $Z_3$ )

are laminated,

wherein the said copolymer based on ethylene/ $\alpha$ -olefin (a-2) is a copolymer of ethylene, an  $\alpha$ -olefin and, optionally incorporated, non-conjugated polyene and has a Mooney viscosity  $ML_{1+4}(100\text{ }^{\circ}\text{C})$  of 90 - 250 and an ethylene content of 70 - 95 mole % and

wherein the said olefinic thermoplastic elastomer composition ( $Z_3$ ) is one which comprises, per 100 parts by weight of an olefinic thermoplastic elastomer (C), at least one kind selected from the group consisting of 0.5 - 25 parts by weight of an organopolysiloxane (D), 0.5 - 10 parts by weight of a fluorine-containing polymer (E) and 0.5 - 10 parts by weight of an antistatic agent (F), each in a proportion given above, and which further comprises a polyolefin resin (G) in an amount of 5 - 200 parts by weight.

**【 CLAIM 5 】** The foamed laminate based on olefin as claimed in any one of claims 2 to 4, wherein the olefinic thermoplastic elastomer component (C) is one which is obtained by a dynamic heat treatment of a mixture comprising a crystalline polyolefin resin (c-1) and a rubber (c-2).

**【 CLAIM 6 】** The foamed laminate based on olefin as claimed in claim 3 or 4, wherein the polyolefin resin (G) is an ultrahigh molecular weight polyolefin resin (Y).

**【 CLAIM 7 】** The formed laminate based on olefin as claimed in claim 1, 3, 4 or 6, wherein the ultrahigh molecular weight polyolefin resin (Y)



comprises 15 - 40 parts by weight of an ultrahigh molecular weight polyolefin resin (y-1) having an intrinsic viscosity ( $\eta$ ) of 10 - 40 dl/g as determined in decalin at 135 °C and 85 - 60 parts by weight of a polyolefin resin (y-2) having an intrinsic viscosity ( $\eta$ ) of 0.1 - 5 dl/g as determined in decalin at 135 °C, with the said constituents (y-1) and (y-2) summing up to 100 parts by weight.

【 CLAIM 8 】 The foamed laminate based on olefin as claimed in any one of claims 1 to 7, wherein the ethylenic thermoplastic elastomer (A) comprises a polypropylene resin (a-3) in an amount of 30 parts by weight or less, per 100 parts by weight of total sum of the polyethylene resin (a-1) and the copolymer based on ethylene/ $\alpha$ -olefin (a-2).

【 CLAIM 9 】 The foamed laminate based on olefin as claimed in any one of claims 1 to 8, wherein the foaming agent (B) is an organic or inorganic foaming agent of a thermal decomposition type.

【 CLAIM 10 】 The foamed laminate based on olefin as claimed in any one of claims 1 to 9, wherein the content of the foaming agent (B) is 0.5 - 20 parts by weight per 100 parts by weight of the ethylenic thermoplastic elastomer (A).

【 CLAIM 11 】 The foamed laminate based on olefin, as claimed in any one of claims 1 to 10, wherein the foaming expansion ratio of the foamed body ( $X_2$ ) is at least twofold.

【 CLAIM 12 】 The foamed laminate based on olefin as claimed in any one of claims 1 to 11, wherein

the ethylenic thermoplastic elastomer (A) consists of a thermoplastic elastomer obtained by subjecting a mixture of the polyethylene resin (a-1) and the copolymer based on ethylene/ $\alpha$ -olefin (a-2) or a mixture which contains further, on requirement, the polypropylene resin (a-3) to a dynamic heat treatment in the absense of cross-linking agent.

【CLAIM 13】 The foamed laminate based on olefin as claimed in any one of claims 2 to 4, wherein the olefinic thermoplastic elastomer (C) is one which is obtained by subjecting a mixture comprising the crystalline polyolefin resin (c-1) and the rubber (c-2) to a dynamic heat treatment in the presence of a cross-linking agent.

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**【 DETAILED DESCRIPTION OF THE INVENTION 】****【 0001 】****【 TECHNICAL FIELD OF THE INVENTION 】**

The present invention relates to a foamed laminate based on olefin, in which a foamed body of an ethylenic thermoplastic elastomer is used for the substrate layer and an ultrahigh molecular weight polyolefin resin or an olefinic thermoplastic elastomer composition is used for the skin layer.

**【 0002 】****【 PRIOR ART 】**

As a technique for producing foamed articles of elastomer (vulcanized rubber), a process has hitherto been known, in which a vulcanizing agent and a foaming agent are admixed to natural rubber or a synthetic rubber and kneaded, whereupon the resulting kneaded mass is formed into a contemplated shape, followed by heating to effect vulcanization and foaming to obtain a foamed article of elastomer.

By the above-mentioned prior technique, however, it is necessary for forming the said rubber into a predetermined shape by continuous extrusion to perform preliminarily a process step of kneading a composite blend together with the rubber to obtain the kneaded mass before the continuous extrusion and to carry out thereafter a process step of forming the kneaded mass into a form of ribbon preliminarily for facilitation of easy supply of the kneaded mass to the extruding machine before the continuous kneading. Thus, the prior technique as given above is disadvantageous in the

industrial production, since the production process steps are intricate and, in addition, considerable time is required for both the process steps of vulcanization and of foaming.

【 0003 】

As a technique for solving such problems, there is a method of using, for example, a thermoplastic resin, such as an ethylene/vinyl acetate copolymer, low density polyethylene or so on, or a partially cross-linked thermoplastic elastomer constituted of an olefinic copolymer rubber and an olefinic resin. According to this method, the process steps mentioned above can be dispensed with.

【 0004 】

However, thermoplastic resins and thermoplastic elastomers conventionally used have problems that inferior appearance may be apt to occur due to the tendency to occurrence of defoaming upon the foaming molding and that the foaming expansion ratio of the foamed article is lower, as amounting only to about 1.5 times, whereby a harder hand touch will result.

Further, when a part element subject to repeated sliding or a partial component subject to contact with human or materials, such as weather strip or sealing element on window sash for automobile, is produced from a conventional foamed body, it may difficultly be served for practical use as a sliding element or the like by inferior durability thereof due to the poor resistance to abrasion and lower sliding performance thereof.

【 0005 】

**【 SUBJECT TO BE SOLVED BY THE INVENTION 】**

An object of the present invention is to solve the problems concomitant with the prior technique mentioned above and to provide a foamed laminate based on olefin which is made of an olefinic polymer premitting recycled use and obtainable at a high foaming expansion ratio and, thus, exhibits a soft hand touch and which is superior in the appearance, in the resistance to abrasion, in the durability and in the sliding performance.

**【 0006 】**

**【 MEANS FOR SOLVING THE SUBJECT 】**

The present invention resides in the following foamed laminate based on olefin:

(1) A foamed laminate based on olefin in which

a substrate layer, consisting of a foamed body ( $X_2$ ) of a foamable ethylenic thermoplastic elastomer composition ( $X_1$ ) comprising the ethylenic thermoplastic elastomer (A) and the foaming agent (B), said ethylenic thermoplastic elastomer (A) comprising 5 - 60 parts by weight of a polyethylene resin (a-1) and 40 - 95 parts by weight of a copolymer based on ethylene/ $\alpha$ -olefin (a-2), with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, and

a skin layer made of an ultrahigh molecular weight polyolefin resin (Y)

are laminated,

wherein the said copolymer based on ethylene/ $\alpha$ -olefin (a-2) is a copolymer of ethylene, an  $\alpha$ -olefin and, optionally incorporated, non-conjugated polyene and has a Mooney viscosity  $ML_{1+4}(100\text{ }^{\circ}\text{C})$  of 90

- 250 and an ethylene content of 70 - 95 mole % and wherein the said ultrahigh molecular weight polyolefin resin (Y) is one which has an intrinsic viscosity ( $\eta$ ) of 3.5 - 8.3 dl/g as determined in decalin at 135 °C .

(2) A foamed laminate based on olefin in which a substrate layer, consisting of a foamed body ( $X_2$ ) of a foamable ethylenic thermoplastic elastomer composition ( $X_1$ ) comprising the ethylenic thermoplastic elastomer (A) and the foaming agent (B), said ethylenic thermoplastic elastomer (A) comprising 5 - 60 parts by weight of a polyethylene resin (a-1) and 40 - 95 parts by weight of a copolymer based on ethylene/ $\alpha$ -olefin (a-2), with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, and

a skin layer made of an olefinic thermoplastic elastomer composition ( $Z_1$ )

are laminated,

wherein the said copolymer based on ethylene/ $\alpha$ -olefin (a-2) is a copolymer of ethylene, an  $\alpha$ -olefin and, optionally incorporated, non-conjugated polyene and has a Mooney viscosity  $ML_{1+4}(100\text{ }^\circ\text{C})$  of 90 - 250 and an ethylene content of 70 - 95 mole % and

wherein the said olefinic thermoplastic elastomer composition ( $Z_1$ ) is one which comprises, per 100 parts by weight of an olefinic thermoplastic elastomer (C), at least one kind selected from the group consisting of 0.5 - 25 parts by weight of an organopolysiloxane (D), 0.5 - 10 parts by weight of a fluorine-containing polymer (E) and 0.5 - 10 parts by weight of an antistatic agent (F), each

in a proportion as given above.

(3) A foamed laminate based on olefin in which

a substrate layer, consisting of a foamed body ( $X_2$ ) of a foamable ethylenic thermoplastic elastomer composition ( $X_1$ ) comprising the ethylenic thermoplastic elastomer (A) and the foaming agent (B), said ethylenic thermoplastic elastomer (A) comprising 5 - 60 parts by weight of a polyethylene resin (a-1) and 40 - 95 parts by weight of a copolymer based on ethylene/ $\alpha$ -olefin (a-2), with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, and

a skin layer made of an olefinic thermoplastic elastomer composition ( $Z_2$ )

are laminated,

wherein the said copolymer based on ethylene/ $\alpha$ -olefin (a-2) is a copolymer of ethylene, an  $\alpha$ -olefin and, optionally incorporated, non-conjugated polyene and has a Mooney viscosity  $ML_{1+4}(100^\circ\text{C})$  of 90 - 250 and an ethylene content of 70 - 95 mole % and

wherein the said olefinic thermoplastic elastomer composition ( $Z_2$ ) is one which comprises, per 100 parts by weight of an olefinic thermoplastic elastomer (C), a polyolefin resin (G) in an amount of 5 - 200 parts by weight.

(4) A foamed laminate based on olefin in which

a substrate layer, consisting of a foamed body ( $X_2$ ) of a foamable ethylenic thermoplastic elastomer composition ( $X_1$ ) comprising the ethylenic thermoplastic elastomer (A) and the foaming agent (B), said ethylenic thermoplastic elastomer (A) comprising 5 - 60 parts by

weight of a polyethylene resin (a-1) and 40 - 95 parts by weight of a copolymer based on ethylene/ $\alpha$ -olefin (a-2), with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, and

a skin layer made of an olefinic thermoplastic elastomer composition ( $Z_3$ )

are laminated,

wherein the said copolymer based on ethylene/ $\alpha$ -olefin (a-2) is a copolymer of ethylene, an  $\alpha$ -olefin and, optionally incorporated, non-conjugated polyene and has a Mooney viscosity  $ML_{1+4}(100\text{ }^{\circ}\text{C})$  of 90 - 250 and an ethylene content of 70 - 95 mole % and

wherein the said olefinic thermoplastic elastomer composition ( $Z_3$ ) is one which comprises, per 100 parts by weight of an olefinic thermoplastic elastomer (C), at least one kind selected from the group consisting of 0.5 - 25 parts by weight of an organopolysiloxane (D), 0.5 - 10 parts by weight of a fluorine-containing polymer (E) and 0.5 - 10 parts by weight of an antistatic agent (F), each in a proportion given above, and further comprises a polyolefin resin (G) in an amount of 5 - 200 parts by weight.

(5) The foamed laminate based on olefin as defined in any one of the above (2) to (4), wherein the olefinic thermoplastic elastomer component (C) is one which is obtained by a dynamic heat treatment of a mixture comprising a crystalline polyolefin resin (c-1) and a rubber (c-2).

(6) The foamed laminate based on olefin as defined in the above (3) or (4), wherein the polyolefin resin (G)



is an ultrahigh molecular weight polyolefin resin (Y).

(7) The formed laminate based on olefin as defined in the above (1), (3), (4) or (6), wherein the ultrahigh molecular weight polyolefin resin (Y) comprises 15 - 40 parts by weight of an ultrahigh molecular weight polyolefin resin (y-1) having an intrinsic viscosity ( $\eta$ ) of 10 - 40 dl/g as determined in decalin at 135 °C and 85 - 60 parts by weight of a polyolefin resin (y-2) having an intrinsic viscosity ( $\eta$ ) of 0.1 - 5 dl/g as determined in decalin at 135 °C, with the said constituents (y-1) and (y-2) summing up to 100 parts by weight.

(8) The foamed laminate based on olefin as defined in any one of the above (1) to (7), wherein the ethylenic thermoplastic elastomer (A) comprises a polypropylene resin (a-3) in an amount of 30 parts by weight or less, per 100 parts by weight of total sum of the polyethylene resin (a-1) and the copolymer based on ethylene/ $\alpha$ -olefin (a-2).

(9) The foamed laminate based on olefin as defined in any one of the above (1) to (8), wherein the foaming agent (B) is an organic or inorganic foaming agent of a thermal decomposition type.

(10) The foamed laminate based on olefin as defined in any one of the above (1) to (9), wherein the content of the foaming agent (B) is 0.5 - 20 parts by weight per 100 parts by weight of the ethylenic thermoplastic elastomer (A).

(11) The foamed laminate based on olefin, as defined in any one of the above (1) to (10), wherein the foaming expansion ratio of the foamed body ( $X_2$ ) is at least

twofold.

(12) The foamed laminate based on olefin as defined in any one of the above (1) to (11), wherein the ethylenic thermoplastic elastomer (A) consists of a thermoplastic elastomer obtained by subjecting a mixture of the polyethylene resin (a-1) and the copolymer based on ethylene/ $\alpha$ -olefin (a-2) or a mixture which contains further, on requirement, the polypropylene resin (a-3) to a dynamic heat treatment in the absence of cross-linking agent.

(13) The foamed laminate based on olefin as defined in any one of the above (2) to (4), wherein the olefinic thermoplastic elastomer (C) is one which is obtained by subjecting a mixture comprising the crystalline polyolefin resin (c-1) and the rubber (c-2) to a dynamic heat treatment in the presence of a cross-linking agent.

【 0007 】

○ The ethylenic thermoplastic elastomer (A)

The ethylenic thermoplastic elastomer (A) to be used as a raw material of the substrate layer according to the present invention is composed of 5 - 60 parts by weight, preferably 10 - 50 parts by weight, of a polyethylene resin (a-1) and 40 - 94 parts by weight, preferably 50 - 90 parts by weight, of a copolymer based on ethylene/ $\alpha$ -olefin (a-2), wherein the total of the components (a-1) and (a-2) sums up to 100 parts by weight. The ethylenic thermoplastic elastomer (A) may contain, if necessary, a polypropylene resin (a-3).

【 0008 】

The ethylenic thermoplastic elastomer (A) to be used

according to the present invention may preferably be an olefinic thermoplastic elastomer obtained by subjecting a mixture containing the polyethylene resin (a-1) and the copolymer based on ethylene/ $\alpha$ -olefin (a-2) in the above-mentioned proportion or a mixture containing further, on requirement, the polypropylene resin (a-3) to a dynamic heat treatment in the absence of cross-linking agent, as will be described afterwards. When the contents of the polyethylene resin (a-1) and of the copolymer based on ethylene/ $\alpha$ -olefin (a-2) are in the above-mentioned ranges, a superior rubbery elasticity is revealed.

【 0009 】

As the polyethylene resin (a-1) to be used according to the present invention, known ones, such as high density polyethylene, medium density polyethylene, linear low density polyethylene and low density polyethylene, may be employed without any restriction, wherein a linear low density polyethylene is preferred and, in particular, a linear low density polyethylene obtained by polymerization using a metallocene catalyst is preferred.

【 0010 】

The polyethylene resin (a-1) may favorably have a melt flow rate (MFR; ASTM D-1238, 190 °C, 2.16 kg load) of 0.01 - 100 g/10 min., preferably 0.01 - 50 g/10 min. An ultrahigh molecular weight polyethylene having an MFR lower than 0.1 g/10 min. has usually an intrinsic viscosity ( $\eta$ ) of 7 - 40 dl/g, as determined in decalin (decahydronaphthalene) at 135 °C. When such an

ultrahigh molecular weight polyethylene is used as the polyethylene resin (a-1), it is favorable to use it in a form of an ultrahigh molecular weight resin composition comprising 15 - 40 % by weight of a polyethylene of from lower to higher molecular weight having an intrinsic viscosity ( $\eta$ ) of 0.1 - 5 dl/g, as determined in decalin at 135 °C, and 85 - 60 % by weight of an ultrahigh molecular weight polyethylene having an intrinsic viscosity ( $\eta$ ) of 7 - 40 dl/g, wherein the ultrahigh molecular weight polyethylene resin composition may preferably have, as a whole, an intrinsic viscosity ( $\eta$ ) of 3.5 - 8.3 dl/g.

【 0011 】

The polyethylene resin (a-1) may favorably have a density of 0.880 - 0.980 g/cm<sup>3</sup>, preferably 0.900 - 0.950 g/cm<sup>3</sup>.

In case a linear low density polyethylene is used as the polyethylene resin (a-1), it is favorable to use a linear low density polyethylene having an MFR (ASTM D-1238, 190 °C, 2.16 kg load) of 0.1 - 30 g/10 min, preferably 0.2 - 20 g/10 min., and a density of 0.880 - 0.950 g/cm<sup>3</sup>, preferably 0.910 - 0.940 g/cm<sup>3</sup>.

【 0012 】

When a linear low density polyethylene is used as the polyethylene resin (a-1), a substrate layer with scarce tendency to occurrence of surface roughness and to formation of adherent surface, as compared with the case where a high density polyethylene or a medium density polyethylene is used, can be obtained.

【 0013 】

The polyethylene resin (a-1) may be either a homopolymer of ethylene or a copolymer of ethylene with small proportion, such as for example, 10 mole % or less, of other comonomer. For such other comonomer, there may be exemplified  $\alpha$ -olefins having 3 - 20 carbon atoms, preferably 3 - 8 carbon atoms, and vinyl monomers, such as vinyl acetate and ethyl acrylate. As the  $\alpha$ -olefin to be used for such other comonomer, there may be exemplified propylene, 1-butene, 4-methyl-1-pentene, 1-hexene and 1-octene. These other comonomers may be used either individually or in a combination of two or more of them.

The polyethylene resin (a-1) may be used either individually or in a combination of two or more.

【 0014 】

The copolymer based on ethylene/ $\alpha$ -olefin (a-2) to be used according to the present invention may be one which has a Mooney viscosity  $ML_{1+4}(100\text{ }^{\circ}\text{C})$  of 90 - 250, preferably 100 - 200, more preferably 110 - 180, and an ethylene content of 70 - 90 mole %, preferably 75 - 90 mole %, more preferably 75 - 85 mole %. Here, the ethylene content does mean a content of ethylene with respect to the total  $\alpha$ -olefins (inclusive of also ethylene).

【 0015 】

The copolymer based on ethylene/ $\alpha$ -olefin (a-2) may either be a copolymer constituted of ethylene and an  $\alpha$ -olefin having 3 - 20 carbon atoms, preferably 3 - 8 carbon atoms, or may further contain co-polymerized comonomer(s) other than the  $\alpha$ -olefin. For the

comonomer(s) other than the  $\alpha$ -olefin, there may be exemplified non-conjugated polyenes and the like. The copolymer based on ethylene/ $\alpha$ -olefin (a-2) may be either a random copolymer or a block-copolymer.

【 0016 】

For concrete ones of the copolymer based on ethylene/ $\alpha$ -olefin (a-2), there may be recited, for example, ethylene/ $\alpha$ -olefin copolymers and ethylene/ $\alpha$ -olefin/non-conjugated polyene copolymers. Among them, preference is given to ethylene/ $\alpha$ -olefin/non-conjugated polyene copolymers.

In the copolymers based on ethylene/ $\alpha$ -olefin (a-2), there may be recited for the  $\alpha$ -olefin to be co-polymerized with ethylene, for example, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene and 1-octene. Such  $\alpha$ -olefins may be used either each solely or in a combination of two or more of them.

【 0017 】

In the copolymer based on ethylene/ $\alpha$ -olefin (a-2), there may be enumerated as the non-conjugated polyene to be co-polymerized with ethylene and the  $\alpha$ -olefin, for example, non-conjugated dienes, such as dicyclopentadiene, 1,4-hexadiene, cyclooctadiene, methylenenorbornene and ethylenenorbornene. The non-conjugated polyenes may be used either each alone or in a combination of two or more of them. The copolymer of ethylene/ $\alpha$ -olefin/non-conjugated polyene has usually an iodine value of 0.1 - 50, preferably 5 - 30.

The copolymer based on ethylene/ $\alpha$ -olefin (a-2) may

be used either individually or in a combination of two or more kinds.

【 0018 】

For the polypropylene resin (a-3), known polypropylene resins may be used without any restriction. Concretely, the polypropylene resins etc. given below may be exemplified:

- 1) Homopolymers of propylene,
  - 2) Random copolymers of 90 mole % or more of propylene with less than 10 mole % of other  $\alpha$ -olefin (random copolymer of propylene/ $\alpha$ -olefin)
- and
- 3) Block-copolymers of 70 mole % or more of propylene with less than 30 mole % of other  $\alpha$ -olefin (block-copolymer of propylene/ $\alpha$ -olefin).

As the said other  $\alpha$ -olefin to be co-polymerized with propylene, there may be enumerated concretely, for example,  $\alpha$ -olefins having 2 - 20 carbon atoms, preferably 2 - 8 carbon atoms, such as ethylene, 1-butene, 4-methyl-1-pentene, 1-hexene and 1-octene.

【 0019 】

For the polypropylene resins (a-3), the above-mentioned homopolymers of propylene 1) and the random copolymers of propylene/ $\alpha$ -olefin 2) are preferable, wherein those which have MFRs (ASTM D-1238, 230 °C, 2.16 kg load) of 0.1 - 50 g/10 min. are particularly preferred.

The polypropylene resins (a-3) may be used either each individually or in a combination of two or more of them.

## 【 0020 】

The content of the polypropylene resin (a-3) in the ethylenic thermoplastic elastomer (A) to be used according to the present invention may favorably be, in general, 30 parts by weight or less, preferably 2 - 30 parts by weight, more preferably 5 - 20 parts by weight, per 100 parts by weight of the total amount of the polyethylene resin (a-1) and the copolymer based on ethylene/ $\alpha$ -olefin (a-2).

When the content of the polypropylene resin (a-3) is in the above-mentioned range, the substrate layer obtained will be superior in the appearance due to scarce tendency to occurrence of surface roughness and, in addition, reveals a scarce sticky touch.

## 【 0021 】

The ethylenic thermoplastic elastomer (A) to be used according to the present invention is superior in the rubbery elasticity even without being subjected to cross linking (vulcanization) using a cross-linking agent and cross-linking assistant. The ethylenic thermoplastic elastomer (A) to be used according to the present invention is not an elastomer of conventional thermosetting type, such as vulcanized rubber, but is a thermoplastic elastomer and permits easily recycled utilization. It does require no use of cross-linking agent and permits, thus, to dispense with a working step of kneading of such cross-linking agent, whereby it can be obtained simply and efficiently by recourse to one single process step of dynamic heat treatment and thus at a lower price.



## 【 0022 】

The ethylenic thermoplastic elastomer (A) to be used according to the present invention may contain, on requirement, various known additives, such as softening agent, heat-resisting stabilizer, antioxidant, weathering stabilizer, antistatic agent, filler, coloring agent and lubricant, in amounts within the range not obstructing the purpose of the present invention.

As the softening agent to be compounded with the ethylenic thermoplastic elastomer (A) according to the present invention, a softening agent based on mineral oil may favorably be used. For such a softening agent based on mineral oil, it is favorable to use a paraffinic, naphthenic or aromatic softening agent which is used usually in rubbers.

## 【 0023 】

## ○ Production of ethylenic thermoplastic elastomer (A)

The ethylenic thermoplastic elastomer (A) to be used according to the present invention can be produced by mixing the polyethylene resin (a-1), the copolymer based on ethylene/ $\alpha$ -olefin (a-2) and resins and additives to be incorporated on requirement in the specific proportion mentioned previously and subjecting the resulting mixture to a dynamic heat treatment.

## 【 0024 】

The word "dynamic heat treatment" means that the polyethylene resin (a-1), the copolymer based on ethylene/ $\alpha$ -olefin (a-2) and the resins and additives to be blended on requirement are kneaded in a molten (fused) state. The dynamic heat treatment can be performed

using a kneading apparatus, such as a mixing roll, an intensive mixer (for instance, Bumbury's mixer or kneader), a single shaft extruder or a double shaft extruder, wherein preference is given to the use of double shaft extruder. The dynamic heat treatment may favorably be carried out in a non-open type kneading apparatus. It is also favorable to work under an inert gas, such as nitrogen.

#### 【 0025 】

On carrying out the dynamic heat treatment, it is favorable to settle a condition of a kneading temperature usually at 150 - 280 °C, preferably 170 - 240 °C, and a kneading duration usually of 1 - 20 minutes, preferably 1 - 5 minutes. The shearing force to be imposed upon the kneading may favorably be settled, in general, at  $10 - 10^4 \text{ sec}^{-1}$ , preferably  $10^2 - 10^4 \text{ sec}^{-1}$ , in terms of shearing velocity.

#### 【 0026 】

It is favorable for carrying out the dynamic heat treatment using a double shaft extruder that the condition of the following inequality (1), preferably inequality (1'), more preferably inequality (1''), is satisfied:

#### 【 Formula 1 】

$$4.8 < \left[ \{(T-130)/100\} + 2.2 \cdot \log P + \log Q - \log R \right]$$

$$< 7.0 \quad \dots\dots (1)$$

$$5.0 < \left[ \{(T-130)/100\} + 2.2 \cdot \log P + \log Q - \log R \right]$$

$$< 6.8 \quad \dots\dots (1')$$

$$5.3 < \left[ \{(T-130)/100\} + 2.2 \cdot \log P + \log Q - \log R \right]$$

$$< 6.5 \quad \dots\dots (1'')$$

In the above inequalities (1), (1') and (1''), T denotes the resin temperature at the die exit of the double shaft extruder and P, Q and R represent each the screw diameter (mm), the maximum shearing velocity appeared ( $\text{sec}^{-1}$ ) and the extrusion throughput (kg/hr) of the extruder, respectively. The maximum shearing velocity Q in  $\text{sec}^{-1}$  can be determined by the equation

$$Q = (P \times \pi \times S) / U$$

in which P is the screw diameter in mm, S denotes the revolution rate of the screw per second (rps) and U denotes the distance in mm of the clearance between the inside face of the barrel wall and the kneading segment of the screw at its narrowest portion.

【 0027 】

The ethylenic thermoplastic elastomer (A) obtained by the dynamic heat treatment performed using a double shaft extruder in the absence of cross-linking agent under the condition satisfying the above inequality (1) is superior in the tensile strength, in the permanent elongation, in the compression set and in the molding appearance.

By the process for producing the ethylenic thermoplastic elastomer (A) according to the present invention, it is possible to produce the ethylenic thermoplastic elastomer (A) exhibiting superior rubbery elasticity in a simple and efficient manner by one single process step, by mixing the polyethylene resin (a-1) and the copolymer based on ethylene/ $\alpha$ -olefin (a-2) or mixing the polyethylene resin (a-1), the copolymer based on ethylene/ $\alpha$ -olefin (a-2) and the resins and additives

blended on requirement in the above-mentioned specific proportion and subjecting the resulting mixture to the dynamic heat treatment, even when a cross-linking agent, such as an organic peroxide, and a cross-linking assistant, such as a divinyl compound used conventionally in the production of vulcanized rubber are not incorporated. No cross-linking agent nor cross-linking assistant is required and there is no necessity of bothersome vulcanization step, whereby the production can be effected at a low cost.

【 0028 】

○ The foaming agent (B)

As the foaming agent (B) to be blended to the raw material of the substrate layer, there may be recited, for example, organic and inorganic thermal decomposition type foaming agents; water; solvents, such as those based on hydrocarbon and halogenated hydrocarbon; and gases, such as nitrogen gas, carbon dioxide gas, propane and butane. As the foaming agent (B), organic and inorganic thermal decomposition type foaming agents, water, carbon dioxide and so on are preferred.

【 0029 】

As the inorganic foaming agent of thermal decomposition type, there may be recited concretely, for example, sodium hydrogencarbonate, sodium carbonate, ammonium hydrogencarbonate, ammonium carbonate and ammonium nitrite.

As the organic foaming agent of thermal decomposition type, there may be recited concretely, for example, nitroso compounds, such as

N,N'-dimethyl-N,N'-dinitrosoterephtharamide and N,N'-dinitrosopenta-methylenetetramine (DPT); azo compounds, such as azodicarbonamide (ADCA), azobisisobutyronitrile (AZBN), azobiscyclohexylnitrile, azodiaminobenzene and barium azodicarboxylate; sulfonylhydrazides, such as benzenesulfonylhydrazide (BSH), toluenesulfonylhydrazide (TSH), p,p'-oxybis(benzenesulfonylhydrazide) (OBSh) and diphenylsulfon-3,3'-disulfonylhydrazide; and azides, such as calcium azide, 4,4'-diphenyldisulfonyl azide and p-toluenesulfonyl azide.

【 0030 】

The foaming agent (B) may be used individually or in a combination of two or more kinds.

The foaming agent (B) may favorably be used usually in an amount of 0.5 - 20 parts by weight, preferably 1 - 10 parts by weight, per 100 parts by weight of the ethylenic thermoplastic elastomer (A).

【 0031 】

The foamable ethylenic thermoplastic elastomer composition ( $X_1$ ) may, on requirement, contain by admixing thereto a foaming assistant. As the foaming assistant, there may be incorporated metal-containing compounds having a metal, such as zinc, calcium, lead, iron or barium; organic acids, such as citric acid, salicylic acid, phthalic acid, stearic acid and oxalic acid; and urea and its derivatives. The foaming assistant may favorably be used usually in an amount of 0.1 - 20 parts by weight, preferably 1 - 10 parts by weight, per 100 parts by weight of the ethylenic

thermoplastic elastomer (A). The foaming assistant provides functions for, for example, lowering the decomposition temperature of the foaming agent, accelerating the decomposition and forming homogeneous foams.

【 0032 】

The foamable ethylenic thermoplastic elastomer composition ( $X_1$ ) may contain, if necessary, by admixing thereto, for example, an inorganic porous powdery substance, such as zeolite, a resin exhibiting higher adsorptivity for inorganic gases, such as polycarbonate resin, and nucleating agent for foaming.

【 0033 】

The foamable ethylenic thermoplastic elastomer composition ( $X_1$ ) may further contain, if necessary, by admixing thereto, various known additives, for example, filler, heat resisting stabilizer, antioxidant, weathering stabilizer, antistatic agent, wetting agent, lubricant, such as metal soap or wax, pigment, dyestuff, fire retarding agent and blocking inhibitor, within the range not obstructing the purpose of the present invention.

【 0034 】

As the filler to be blended with the ethylenic thermoplastic elastomer composition ( $X_1$ ), those which are incorporated usually in rubbers may favorably be used. Concretely, there may be recited, for example, calcium carbonate, calcium silicate, clay, kaolin, talc, silica, diatomaceous earth, powdery mica, asbestos, barium sulfate, aluminum sulfate, calcium sulfate, magnesium carbonate, molybdenum disulfide, glass fiber,

glass beads, Shirasu balloon, graphite and alumina.

The filler may favorably be incorporated usually in an amount of 40 parts by weight or less, preferably 1 - 30 parts by weight, per 100 parts by weight of the ethylenic thermoplastic elastomer (A).

【 0035 】

○ Preparation of the foamable ethylenic thermoplastic elastomer composition ( $X_1$ )

The foamable ethylenic thermoplastic elastomer composition ( $X_1$ ) can be prepared by compounding the ethylenic thermoplastic elastomer (A), the foaming agent (B) and the optionally employed ingredients, such as foaming assistant and wetting agent.

【 0036 】

For the practical way of compounding the ethylenic thermoplastic elastomer (A) and the foaming agent (B), there may be exemplified a method in which a pelletized product of the ethylenic thermoplastic elastomer (A) is once kneaded together with the foaming agent (B) on, for example, a tumbler type Bravender, a V-shaped Bravender, a ribbon blender or a Henschel mixer, followed by, if necessary, further kneading on an open type mixing roll or on a non-open type machine, such as Bumbury's mixer, extruder, kneader or continuous mixer.

The weathering stabilizer, heat-resisting stabilizer, antioxidant, pigment, dyestuff and so on may be admixed at any process step given above.

【 0037 】

The substrate layer according to the present invention is a foamed body ( $X_2$ ) of the above-mentioned foamable

ethylenic thermoplastic elastomer composition ( $X_1$ ) and can be obtained, for example, by a method of heating the ethylenic thermoplastic elastomer composition ( $X_1$ ).

【 0038 】

For the raw material of the skin layer, at least one kind selected from the raw materials based on olefin given in the following 1) to 4) may be employed according to the present invention:

1) The ultrahigh molecular weight polyolefin resin (Y) mentioned previously which is an ultrahigh molecular weight polyolefin resin having an intrinsic viscosity ( $\eta$ ) of 3.5 - 8.3 dl/g, as determined in decalin of 135 °C .

2) An olefinic thermoplastic elastomer composition ( $Z_1$ ) containing, per 100 parts by weight of the olefinic thermoplastic elastomer (C), at least one selected from the group consisting of 0.5 - 25 parts by weight of an organopolysiloxane (D), 0.5 - 10 parts by weight of a fluorine-containing polymer (E) and 0.5 - 10 parts by weight of an antistatic agent (F), each in the given proportion.

3) An olefinic thermoplastic elastomer composition ( $Z_2$ ) containing a polyolefin resin (G) in an amount of 5 - 200 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (C).

4) An olefinic thermoplastic elastomer composition ( $Z_3$ ) containing, per 100 parts by weight of the olefinic thermoplastic elastomer (C), at least one selected from the group consisting of 0.5 - 25 parts by weight of an organopolysiloxane (D), 0.5 - 10 parts by weight of a fluorine-containing polymer (E) and 0.5 - 10 parts by



weight of an antistatic agent (F), each in the given proportion, and further a polyolefin resin (G) in an amount of 5 - 200 parts by weight.

【 0039 】

○ The ultrahigh molecular weight polyolefin resin (Y)

The ultrahigh molecular weight polyolefin resin (Y) to be used as the raw material of the skin layer according to the present invention is an ultrahigh molecular weight polyolefin resin having an intrinsic viscosity ( $\eta$ ) in the range from 3.5 to 8.3 dl/g, preferably from 3.8 to 8.0 dl/g, as determined in decalin of 135 °C. The ultrahigh molecular weight polyolefin resin (Y) may either consist of a single kind of resin or a composition comprising two or more resins. For the case of the resin composition, one which has an intrinsic viscosity ( $\eta$ ) as the entire composition within the above-mentioned range may be employed.

【 0040 】

In the case where the ultrahigh molecular weight polyolefin resin (Y) is a resin composition, an ultrahigh molecular weight polyolefin resin composition comprising an ultrahigh molecular weight polyolefin resin (y-1) having an intrinsic viscosity ( $\eta$ ) of 10 - 40 dl/g, as determined in decalin of 135 °C, and a polyolefin resin (y-2) having an intrinsic viscosity ( $\eta$ ) of 0.1 - 5 dl/g, as determined in decalin of 135 °C, is favorable and, further, such an ultrahigh molecular weight polyolefin resin composition may be more favorable, which contains 15 - 40 parts by weight of the ultrahigh molecular weight polyolefin resin (y-1) and 60

- 85 parts by weight of the polyolefin resin (y-2), and particularly favorable one contains 18 - 35 parts by weight of the ultrahigh molecular weight polyolefin resin (y-1) and 65 - 82 parts by weight of the polyolefin resin (y-2), with the total of the two summing up to 100 parts by weight.

【 0041 】

As the ultrahigh molecular weight polyolefin resin (y-1) and the polyolefin resin (y-2), there may be recited, for example, homopolymers and copolymers of  $\alpha$ -olefins, such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 4-methyl-1-pentene and 3-methyl-1-pentene. For the ultrahigh molecular weight polyolefin resin (y-1) and for the polyolefin resin (y-2), copolymers composed mainly of ethylene, namely, homopolymers of ethylene and copolymers of ethylene with other  $\alpha$ -olefin, are preferred.

【 0042 】

The ultrahigh molecular weight polyolefin resin (Y) may contain a liquid or solid softening agent (lubricating oil).

As the liquid softening agent to be admixed to the ultrahigh molecular weight polyolefin resin (Y), those based on mineral oil and synthetic ones are used. Concretely, there may be enumerated, for example, paraffinic and naphthenic lubricant oils, liquid paraffin, spindle oil, refrigerator oil, dynamo oil, turbine oil, machine oil and cylinder oil. As the synthetic lubricant oils, there may be recited concretely synthetic

hydrocarbon oils, polyglycol oils, polyphenyl ether oils, ester oils, phosphate oils, polychlorotrifluoroethylene oils, fluoroester oils, chlorinated biphenyl oils and silicone oils.

【 0043 】

As the solid softening agent, concretely, grafite and molybdenum disulfide are used principally, though otherwise boron nitride, wolfrum disulfide, lead oxide, glass powder, metal soaps and so on may also be used.

The softening agent may be incorporated either individually or in a combination of two or more kinds in a form of, for example, powder, sol, gel or suspensoid.

【 0044 】

The content of the softening agent may favorably be in the range from 1 to 20 parts by weight, preferably from 3 to 15 parts by weight, per 100 parts by weight of the ultrahigh molecular weight polyolefin resin (Y).

There may be compounded with the ultrahigh molecular weight polyolefin resin (Y), if necessary, additives, such as heat-resisting stabilizer, antistatic agent, weathering stabilizer, antioxidant, filler, coloring agent and lubricant, within the range not obstructing the purpose of the present invention.

【 0045 】

○ The olefinic thermoplastic elastomer compositions (Z<sub>1</sub>) to (Z<sub>3</sub>)

○ The olefinic thermoplastic elastomer (C)

According to the present invention, there may be incorporated, for the olefinic thermoplastic elastomer (C) to be used as the raw material of the skin layer, for

example, an olefinic thermoplastic elastomer composed of a crystalline polyolefin resin (c-1) and a rubber (c-2).

【 0046 】

As the crystalline polyolefin resin (c-1), there may be enumerated, for example, homopolymers and copolymers of  $\alpha$ -olefins having 2 - 20 carbon atoms. Concrete examples of the crystalline polyolefin (c-1) include (co)polymers given below:

1) Homopolymers of ethylene (obtained either by low pressure and high pressure processes)

2) Copolymers of ethylene with 10 mole % or less, of other  $\alpha$ -olefin or vinyl monomer, such as vinyl acetate or ethyl acrylate

3) Homopolymers of propylene

4) Random copolymers of propylene with 10 mole % or less, of other  $\alpha$ -olefins

5) Block-copolymers of propylene with 30 mole % or less of other  $\alpha$ -olefins

6) Homopolymers of 1-butene

7) Random copolymers of 1-butene with 10 mole % or less, of other  $\alpha$ -olefins

8) Homopolymers of 4-methyl-1-pentene

9) Random copolymers of 4-methyl-1-pentene with 20 mole % or less, of other  $\alpha$ -olefins

As the above  $\alpha$ -olefins, there may concretely be exemplified ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene and 1-octene.

【 0047 】

As the crystalline polyolefin resin (c-1), there may favorably be enumerated homopolymers of propylene and

copolymers of propylene used as principal component with another olefin, for example, propylene/ethylene copolymer, propylene/1-butene copolymer, propylene/1-hexene copolymer and propylene/4-methyl-1-pentene copolymer.

The crystalline polyolefin resin (c-1) may favorably have an MFR (ASTM D-1238, 230 °C, 2.16 kg load) in the range from 0.01 to 100 g/10 min., preferably from 0.1 to 50 g/10 min.

【 0048 】

There is no special limitation as to the rubber (c-2) to be used according to the present invention, though preference is given to olefinic copolymer rubbers.

For the olefinic copolymer rubber to be used as the rubber (c-2), there may be exemplified amorphous random elastomeric copolymers each having, as a main component, an  $\alpha$ -olefin having 2 - 20 carbon atoms, such as non-crystalline  $\alpha$ -olefin copolymers each constituted of at least two  $\alpha$ -olefins and  $\alpha$ -olefin/non-conjugated polyene copolymers each constituted of at least two  $\alpha$ -olefins and non-conjugated diene(s).

【 0049 】

As concrete examples of the olefinic copolymer rubbers to be used as the rubber (c-2), the rubbers, such as those given above may be recited:

1) Copolymer rubbers of ethylene/ $\alpha$ -olefin having ethylene/ $\alpha$ -olefin mole ratios of about 90/10 to 50/50

2) Copolymer rubbers of ethylene/ $\alpha$ -olefin/non-conjugated diene having ethylene/ $\alpha$ -olefin mole ratios of about 90/10 to 50/50

3) Copolymer rubbers of propylene/ $\alpha$ -olefin having the mole ratio propylene/ $\alpha$ -olefin of about 90/10 to 50/50

4) Copolymer rubbers of butene/ $\alpha$ -olefin having butene / $\alpha$ -olefin mole ratios of about 90/10 to 50/50

【 0050 】

As the  $\alpha$ -olefin, there may concretely be exemplified those which are the same as the concretely exemplified  $\alpha$ -olefins constituting the crystalline polyolefin (c-1) given above.

As the non-conjugated dienes, there may concretely be exemplified dicyclopentadiene, 1,4-hexadiene, cyclooctadiene, methylenenorbornene, ethylenenorbornene and so on.

The rubber (c-2) may be used either individually or in a combination of two or more kinds.

【 0051 】

As the rubber (c-2), concretely, there may favorably be used ethylene/propylene copolymer rubbers, ethylene/propylene/non-conjugated polyene copolymer rubbers, ethylene/1-butene copolymer rubbers and ethylene/1-butene/non-conjugated polyene rubbers, with special preference to ethylene/propylene/non-conjugated polyene copolymer rubbers, in particular, ethylene/propylene/ethylenenorbornene copolymer rubber and ethylene/propylene/cyclopentadiene copolymer rubber.

These copolymer rubbers may favorably have Mooney viscosities  $ML_{1+4}(100\text{ }^{\circ}\text{C})$  in the range from 10 to 250, preferably from 40 to 150. For the case where the above

non-conjugated polyene is co-polymerized, they may favorably have iodine values of 25 or lower.

【 0052 】

For the rubber (c-2) to be used according to the present invention, there may also be recited other rubbers, for example, rubbers based on diene, such as styrene/butadiene rubber (SBR), nitrile rubbers (NBR), natural rubber (NR) and butyl rubber (IIR), and SEBS as well as polyisobutylenes.

【 0053 】

In the olefinic thermoplastic elastomer (C) to be used according to the present invention, the weight proportion of the crystalline polyolefin resin (c-1) to the rubber (c-2), namely, [crystalline polyolefin resin]/[rubber], may favorably be in the range of usually from 90/10 to 5/95, preferably from 70/30 to 10/90.

In the case of using, as the rubber (c-2), the olefinic copolymer rubber in combination with other rubber, it is favorable to incorporate the said other rubber in an amount of 40 parts by weight or less, preferably in the range from 5 to 20 parts by weight, per 100 parts by weight of the total sum of the crystalline polyolefin resin (c-1) and the rubber (c-2).

【 0054 】

If necessary, the olefinic thermoplastic elastomer (C) may be compounded with additives, such as softening agent, heat-resisting stabilizer, weathering stabilizer, antioxidant, filler, coloring agent and lubricant, within the range not obstructing the purpose of the present invention.

As the softening agent, those used usually for rubbers may be employed, wherein preference is given to those based on mineral oil and to synthetic ones.

【 0055 】

As the softening agent based on mineral oil to be compounded with the olefinic thermoplastic elastomer (C), for example, lubricating oils based on petroleum, such as paraffinic, naphthenic and aromatic ones, and liquid paraffin are recited. As the synthetic softening agent, there may be recited, for example, polyethylene wax, polypropylene wax, petroleum asphalt and vaseline.

For other softening agents, there may be recited, for example, coal tars, such as coal tar and coal tar pitch; fatty oils, such as castor oil, line seed oil, rape oil, soybean oil and coconut oil; waxes, such as tall oil, beeswax, carnauba wax and lanoline; fatty acids, such as ricinoleic acid, palmitic acid, stearic acid, 12-hydroxystearic acid, montanic acid, oleic acid and erucic acid, as well as their metal salts; synthetic polymer products, such as petroleum resin, cumarone-indene resin and atactic polypropylene; plasticizers based on ester, such as dioctyl phthalate, dioctyl adipate and dioctyl sebacate; others including microcrystalline wax, liquid polybutadiene and modified and hydrogenated products thereof, and liquid Thiokol.

【 0056 】

These softening agents may favorably be used in a proportion of 5 - 200 parts by weight, preferably 15 - 150 parts by weight, more preferably 20 - 80 parts by weight, per 100 parts by weight of the olefinic



thermoplastic elastomer (C).

The softening agent may be added to the olefinic thermoplastic elastomer (C) during the production thereof or may have been admixed beforehand to the rubber (c-2) in a form of an extender oil.

【 0057 】

The olefinic thermoplastic elastomer (C) to be used according to the present invention can be obtained by subjecting a mixture of the polyolefin resin (c-1) and the rubber (c-2), with occasionally incorporated softening agent etc., to the dynamic heat treatment.

The rubber (c-2) may be present in the olefinic thermoplastic elastomer (C) in non-cross-linked state or in every cross-linked state from a partially cross-linked state to the fully cross-linked state.

【 0058 】

For producing the olefinic thermoplastic elastomer (C) in such a cross-linked state, it is favorable to subject a mixture of the polyolefin resin (c-1) and the rubber (c-2) with the optionally added ingredients, such as the softening agent etc., to a dynamic heat treatment in the presence of a cross linking agent.

For the cross linking agent which can be used upon the dynamic heat treatment, those which are used usually in thermosetting type rubbers may be employed, for example, organic peroxides, sulfur, phenol resins, amino resins, quinones and derivatives thereof, compounds based on amine, epoxy compounds and isocyanates. Among them, organic peroxides are especially preferable.

【 0059 】

As the organic peroxide, there may concretely be enumerated, for example, dicumyl peroxide, di-tert-butyl peroxide, 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexane, 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexyne-3, 1,3-bis(tert-butylperoxyisopropyl)benzene, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, n-butyl-4,4-bis(tert-butylperoxy) valerate, benzoyl peroxide, p-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, tert-butylperoxy benzoate, tert-butyl perbenzoate, tert-butylperoxyisopropyl carbonate, diacetyl peroxide, lauroyl peroxide and tert-butylcumyl peroxide.

【 0060 】

Among them, 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexane, 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexyne-3, 1,3-bis(tert-butylperoxyisopropyl)benzene, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane and n-butyl-4,4-bis(tert-butylperoxy) valerate are preferred in view of odour and scorching stability and, in particular, 1,3-bis(tert-butylperoxyisopropyl)benzene is at the most preferable.

According to the present invention, the organic peroxide is used in a proportion of 0.05 - 3 parts by weight, preferably 0.1 - 1 part by weight, per 100 parts by weight of the total sum of the crystalline polyolefin and the rubber.

【 0061 】

On the cross-linking treatment using the organic peroxide, it is possible to add an assistant for the

peroxide cross-linking, such as sulfur, p-quinone dioxime, p,p'-dibenzoylquinonedioxime, N-methyl-N-4-dinitrosoaniline, nitrosobenzene, diphenylguanidine and trimethylolpropane-N,N'-m-phenylenedimaleimide, or to add polyfunctional methacrylate monomers, such as divinylbenzene, triallyl cyanurate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, polyethyleneglycol dimethacrylate, trimethylolpropane trimethacrylate and allyl methacrylate, or poly-functional vinyl monomers, such as vinyl butyrate and vinyl stearate.

【 0062 】

By incorporating the compounds as above, a uniform and mild cross-linking reaction can be expected. In particular, divinylbenzene is at the most preferable according to the present invention. Divinylbenzene is easy to handle, exhibits better compatibility with the principal components, namely, the polyolefin resin (c-1) and the rubber (c-2) and has a function of solubilizing organic peroxide so as to act as a dispersant for the organic peroxide, so that it provides a uniform cross-linking effect by the heat treatment, whereby an olefinic thermoplastic elastomer (C) exhibiting better balance between the flowability and the material properties can be obtained.

【 0063 】

The above-mentioned cross linking assistant or the polyfunctional vinyl monomer may favorably be used in a proportion of 0.1 - 3 % by weight, preferably 0.3 - 2 %

by weight, based on the entire mass to be subjected to the cross linking. When the proportion of the cross linking assistant or the polyfunctional vinyl monomer to be added is in the range given above, the resulting thermoplastic elastomer will be devoid of any residue of unreacted monomer of such cross linking assistant or polyfunctional vinyl monomer, so that no change in the material properties due to the thermal hysteresis occurs upon the process step of molding and superior flowability is attained.

【 0064 】

The word "dynamic heat treatment" means that the components given above are kneaded in a molten state.

As the kneading apparatus, known ones, such as for example, open-type mixing roll and non-open type ones, such as Bumbury's mixer, extruder, kneader and continuous mixer, may be employed. Among them, non-open type kneading apparatuses are preferred, wherein the kneading procedure may favorably be effected under an inert gas atmosphere, such as nitrogen gas or carbon dioxide gas.

【 0065 】

The temperature upon the dynamic heat treatment may usually be at 150 - 280 °C, preferably 170 - 240 °C, and the kneading duration may favorably be 1 - 20 minutes, preferably 3 - 10 minutes. The shearing force imposed may favorably be 100 sec<sup>-1</sup> or greater, preferably 500 - 10,000 sec<sup>-1</sup>, in terms of shearing velocity.

【 0066 】

The olefinic thermoplastic elastomer (C) to be used

favorably according to the present invention may favorably have a gel content, as calculated according to the procedures given below, of 10 % by weight or higher, preferably 20 % by weight or higher, especially preferably 45 % by weight or higher.

【 0067 】

《 Method for determining the gel content 》

About 100 mg of a sample of the thermoplastic elastomer are weighed off and cut into grains of a size of 0.5 mm × 0.5 mm × 0.5 mm and the resulting grains are soaked in 30 ml of cyclohexane in a tightly sealed vessel at 23 °C for 48 hours. The so-soaked granular sample is taken out on a filter paper and is dried at room temperature for over 72 hours until a constant weight is reached.

The value calculated by subtracting the weight of cyclohexane-insoluble ingredients other than the polymer components (for example, fibrous filler, filler and pigments) from the weight of the above dried residual matter is regarded as the "corrected final weight of (Y)".

On the other hand, the value calculated by subtracting the weight of cyclohexane-soluble ingredients other than the polymer components (for example, softening agent) and the weight of cyclohexane-insoluble ingredients other than the polymer components (for example, fibrous filler, filler and pigments) from the weight of the above dried residual matter is regarded as the "corrected initial weight of (X)".

【 0068 】

The gel content (content of cyclohexane-insoluble polymer) is calculated by the equation:

$$\text{Gel cont. (wt. \%)} = \frac{[\text{corrected final wt. (Y)}]}{[\text{corrected init. wt. (X)}]} \times 100$$

【 0069 】

As the olefinic thermoplastic elastomer (C) to be used for the skin layer according to the present invention, the above-mentioned ethylenic thermoplastic elastomer (A) can also be employed.

The olefinic thermoplastic elastomer (C) constituting the skin layer of the foamed laminate based on olefin according to the present invention is constituted of the crystalline polyolefin resin (c-1) and the rubber (c-2) and, therefore, is superior in the flowability.

Such a polyolefinic thermoplastic elastomer (C) can be formed on conventionally employed molding apparatuses by, for example, compression molding, transfer molding, injection molding and extrusion molding.

【 0070 】

○ The organopolysiloxane (D)

As the organopolysiloxane (D) to be used for the raw material of the skin layer according to the present invention, known organopolysiloxanes having -Si-O- bonds in the main chain may be used without any restriction. By incorporating organopolysiloxane (D), a skin layer exhibiting superior sliding performance and superior abrasion resistance can be obtained.

【 0071 】

As the organopolysiloxane (D), there may be recited

concretely, for example, dimethylpolysiloxane, methylphenylpolysiloxane, fluoropolysiloxane, tetramethyl-tetraphenylpolysiloxane and methylhydrogenpolysiloxane, as well as modified polysiloxanes, such as epoxy-modified, alkyl-modified, amine-modified, carboxyl-modified, alcohol-modified, fluorine-modified, alkyl-aralkylpolyether-modified and epoxypolyether-modified ones. Among them, preference is given to dimethylpolysiloxane. The organopolysiloxane (D) can be used either individually or in a combination of two or more kinds.

【 0072 】

For the organopolysiloxane (D), those which have viscosity values (as determined according to JIS K 2283 at 25 °C) in the range from 10 to  $10^7$  cSt are preferred. Among them, those having viscosity values (JIS K 2283 at 25 °C) of  $10^6$  or higher may be formulated as a masterbatch with olefinic resin(s) for enhancing the dispersibility in the olefinic thermoplastic elastomer (C), as they have a very high viscosity. As the olefinic resin to be used here, the crystalline polyolefin resin (c-1) used for preparing the olefinic thermoplastic elastomer (C) is recited and, concretely, there may concretely be recited, for example, homopolymers of ethylene, copolymers of ethylene with other  $\alpha$ -olefins, homopolymers of propylene and copolymers of propylene with other  $\alpha$ -olefins.

【 0073 】

The organopolysiloxane (D) may be incorporated either individually or in a combination of two or more

kinds in accordance with the viscosity thereof. In particular, in the case of using two or more kinds in combination, it is preferable to use a combination of a lower viscosity organopolysiloxane (D) having a viscosity of  $10 - 10^6$  cSt with a higher viscosity organopolysiloxane (D) having a viscosity of  $10^6 - 10^7$  cSt.

【 0074 】

In the olefinic thermoplastic elastomer composition ( $Z_1$ ), the organopolysiloxane (D) may be contained in a proportion of 0.5 - 20 parts by weight, preferably 1 - 18 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (C). If the content of the organopolysiloxane (D) is in the above range, the resulting foamed laminate is superior in the sliding performance and there occurs no inconvenience due to, for example, sticky hand touch of the surface by the organopolysiloxane (D).

【 0075 】

○ The fluorine-containing polymer (E)

As the fluorine-containing polymer (E) to be used according to the present invention, known polymers having fluorine atom may be employed without any restriction. By addition of the fluorine-containing polymer (E), the skin layer becomes superior in the sliding performance and in the abrasion resistance.

As the fluorine-containing polymer (E) to be used according to the present invention, there may be enumerated, for example, polytetrafluoroethylene, tetra-fluoroethylene/hexafluoropropylene copolymer,



tetra-fluoroethylene/perfluorovinyl ether copolymer, tetra-fluoroethylene/ethylene copolymer, polymers of vinylidene fluoride and polymers of vinyl fluoride. The fluorine-containing polymer (E) may be incorporated either individually or in a combination of two or more kinds.

【 0076 】

The fluorine-containing polymer (E) may be formulated preliminarily as a masterbatch with olefinic resin(s) and/or with known inorganic filler(s), in order to facilitate the dispersibility in the olefinic thermoplastic elastomer (C) or to further increase the effect of improving the sliding performance. As the olefinic resin to be used here, those which are the same as used in the masterbatch for the organosiloxane (D) may be enumerated. As the inorganic filler, there may be recited, for example, calcium carbonate, titanium oxide, talc and clay.

【 0077 】

In the olefinic thermoplastic elastomer composition ( $Z_1$ ), the fluorine-containing polymer (E) may be contained in a proportion of 0.5 - 10 parts by weight, preferably 1 - 8 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (C). When the content of the fluorine-containing polymer (E) is in the above range, the resulting foamed laminate is superior in the sliding performance.

【 0078 】

○ The antistatic agent (F)

For the antistatic agent (F) to be used according to

the present invention, known antistatic agents used in general for resins may be employed without any restriction, examples of which include anionic surfactants, cationic surfactants, non-ionic surfactants and ampholytic surfactants. By incorporating the antistatic agent (F), the resulting skin layer becomes superior in the sliding performance and in the abrasion resistance.

【 0079 】

Concrete examples of the antistatic agent (F) include lauryldiethanolamine, N,N-bis(2-hydroxyethyl)-stearylamine, stearyl monoglyceride, distearyl glyceride, tristearyl glyceride, polyoxyethylene-laurylamine capryl ester and stearyldiethanolamine monostearate. The antistatic agent (F) may be used either individually or in a combination of two or more kinds.

【 0080 】

The antistatic agent (F) may be formulated preliminarily as a masterbatch with olefinic resin(s) and/or with known inorganic filler(s), in order to facilitate the dispersibility in the olefinic thermoplastic elastomer (C) or to further increase the effect of improving the sliding abrasion resistance. As the olefinic resin and the inorganic filler to be used here, those which are the same as those mentioned above may be enumerated.

【 0081 】

In the olefinic thermoplastic elastomer composition ( $Z_1$ ), the antistatic agent (F) may be contained in a

proportion of 0.5 - 10 parts by weight, preferably 1 - 8 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (C). When the content of the antistatic agent (F) is in the above range, the resulting foamed laminate is superior in the sliding performance and there occurs no inconvenience due to, for example, whitening by deposition of the antistatic agent (F) on the surface (bleeding out).

【 0082 】

The organopolysiloxane (D), the fluorine-containing polymer (E) and the antistatic agent (F) may each be used either individually or in a combination of two or more kinds, wherein the combination is arbitrary.

【 0083 】

○ The polyolefin resin (G)

As the polyolefin resin (G) to be used according to the present invention, the crystalline polyolefin resin (c-1) used for the olefinic thermoplastic elastomer (C) may favorably be employed. Also, the ultrahigh molecular weight polyolefin resin (Y) described previously may be employed for the polyolefin resin (G) to be used according to the present invention.

【 0084 】

In the olefinic thermoplastic elastomer composition (Z<sub>2</sub>), the polyolefin resin (G) may be contained in a proportion of 5 - 200 parts by weight, preferably 10 - 180 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (C). When the olefinic thermoplastic elastomer (C) and the polyolefin resin (G) are used in such a proportion, the skin layer obtained

exhibits better moldability and better molding appearance and is superior in the sliding performance and in the abrasion resistance.

【 0085 】

The polyolefin resin (G) can be incorporated concurrently with at least one selected from the group consisting of the organopolysiloxane (D), fluorine-containing polymer (E) and the antistatic agent (F). The amount of each component (D) to (G) to be contained in the olefinic thermoplastic elastomer composition (Z<sub>3</sub>) is as given above.

【 0086 】

There may be compounded with the olefinic thermoplastic elastomer compositions (Z<sub>1</sub>) to (Z<sub>3</sub>) to be used for the raw material of the skin layer, on requirement, additives, such as softening agent based on mineral oil, heat resisting stabilizer, weathering stabilizer, antioxidant, filler, coloring agent and lubricant, within the range not obstructing the purpose of the present invention.

【 0087 】

The olefinic thermoplastic elastomer compositions (Z<sub>1</sub>) - (Z<sub>3</sub>) can be produced by known techniques, for example, by kneading the olefinic thermoplastic elastomer (C) with at least one selected from the group consisting of the organopolysiloxane (D), the fluorine-containing polymer (E) and the antistatic agent (F), as well as with the polyolefin resin (G) and other optionally admixed additives.

【 0088 】

The foamed laminate based on olefin according to the present invention is a laminate produced by laminating a skin layer made of the ultrahigh molecular weight polyolefin resin (Y) or the olefinic thermoplastic elastomer compositions ( $Z_1$ ) to ( $Z_3$ ) on a substrate layer made of the foamed body ( $X_2$ ) of the foamable ethylenic thermoplastic elastomer composition ( $X_1$ ) given above. The skin layer may be laminated on the substrate layer covering the entire area or partial area of the substrate layer or it is permissible that other layer(s) is(are) laminated. In the case where skin layer is laminated covering a partial area of the substrate, the residual area not covered by the skin layer may be held exposed. The substrate layer and the skin layer may be laminated using an adhesive, though preferably they are fused together. While there is no special limitation as to the thickness of the foamed laminate, it is favorable that the substrate layer has a thickness of 0.1 - 50 mm, preferably 0.5 - 45 mm, and the skin layer has a thickness of 5  $\mu$ m - 10 mm, preferably 10  $\mu$ m - 8 mm. The foaming expansion ratio of the foamed body ( $X_2$ ) may favorably be in the range from 1.1 to 15 times, preferably from 2 to 10 times the original volume, though there is no special limitation therefor. According to the present invention, even foamed bodies ( $X_2$ ) having higher expansion ratios of 2 times or higher may easily be molded, since the ethylenic thermoplastic elastomer (A) can foam up sufficiently.

【 0089 】

The foamed laminate based on olefin according to the present invention may exhibit a soft hand touch, since

the substrate layer can be made at a high expansion ratio as indicated above and is superior in the appearance, abrasion resistance, durability and sliding performance. The foamed laminate according to the present invention can be produced in an easy manner and reveals a high economical efficiency due to permission of recycled utilization.

【 0090 】

The foamed laminate based on olefin according to the present invention is obtained by providing the substrate layer of the foamed body ( $X_2$ ) of the foamable ethylenic thermoplastic elastomer composition ( $X_1$ ) and making up the skin layer from the ultrahigh molecular weight polyolefin resin (Y) or the olefinic thermoplastic elastomer compositions ( $Z_1$ ) to ( $Z_3$ ) and laminating these layers. The practical manner of lamination may vary according to the shape, size, material properties required and so on, while there may favorably be exemplified a method in which the substrate layer and the skin layer are co-extruded simultaneously using a multilayer extrusion molding machine, followed by heat fusing them together. The ethylenic thermoplastic elastomer composition ( $X_1$ ) foams up upon the heat fusing under co-extrusion to form the foamed body ( $X_2$ ) which build up the substrate layer. Such a heat fusing technique requires no adhesive and permits to obtain a foamed laminate easily by a single process step in an easy manner, wherein the thereby obtained interlayer adhesion between the substrate layer and the skin layer is firm.

【 0091 】

The foamed laminate based on olefin according to the present invention can be used favorably, for example, for automobile parts, such as automobile weather strips, and for architectural materials, such as gaskets. For the automobile weather strips, there may be exemplified door weather strip, hood weather strip, trunk room weather strip, sunroof weather strip, ventilator weather strip and corner strip. As the architectural materials, there may be exemplified gaskets, airtight elements, jointing parts and damper seal at door top. For others, products for leisure and sports, such as golf club grip, grip of baseball bat, swimming fins and diving goggles; protecting cover for hoses; and cushions.

#### 【 0092 】

Fig. 1 shows the sectional construction of one embodiment of an automobile weather strip in which the foamed laminate based on olefin according to the present invention is employed. The automobile weather strip 1 shown in Fig. 1 is constructed from a thin core plate 2 and two contact seal lugs 3 arranged on the core plate 2 in a form of curved fins so as to provide for a tight contact onto the window glass to establish a contact seal. The contact seal lug 3 is made of the foamed laminate based on olefin according to the present invention prepared by laminating the substrate layer 4 and the skin layer 5, wherein the skin layer 5 is disposed on the side for contacting with the window glass.

#### 【 0093 】

#### 【 INVENTIVE EFFECTS 】

The foamed laminate based on olefin according to the

present invention is prepared at a high foaming expansion ratio and provides a soft hand touch and, in addition, it is superior in the appearance, abrasion resistance, durability and sliding performance. The laminate according to the present invention can be produced easily and is easy in the recycled use due to the use of, as the principal raw material, olefinic polymers, providing, thus, a superior economical efficiency.

【 0094 】

#### 【 MODE FOR EMBODYING THE INVENTION 】

Below, the present invention is described in more detail by way of Examples, though the present invention is by no means restricted by these Examples.

【 0095 】

#### Example 1

##### (1) Production of the ethylenic thermoplastic elastomer (A-1)

There were blended on a Henschel mixer 30 parts by weight of a linear low density polyethylene (density =  $0.920/\text{cm}^3$ , MFR = 2.1 g/10 min., ethylene content = 97.0 mole % and 4-methyl-1-pentene content = 3.0 mole %) and 70 parts by weight of an ethylene/propylene/dicyclo-pentadiene copolymer rubber (ethylene content = 77 mole %, Mooney viscosity  $ML_{1+4}(100\text{ }^\circ\text{C}) = 145$  and iodine value = 12). Then, on a double shaft extruder having an L/D of 30 and a screw diameter of 50 mm, a dynamic heat treatment was effected at 200  $^\circ\text{C}$  under a nitrogen atmosphere and the resulting mass was extruded to produce a pelletized



product of an ethylenic thermoplastic elastomer (A-1).

【 0096 】

(2) The ultrahigh molecular weight polyethylene composition (Y-1)

The composition (Y-1) had an intrinsic viscosity ( $\eta$ ) of 7.0 dl/g.

This is an ultrahigh molecular weight polyethylene composition which is composed of an ultrahigh molecular weight polyeththylene resin (y-1) having an intrinsic viscosity ( $\eta$ ) of 28 dl/g as determined in decalin at 135 °C and a polyethylene resin (y-2) having an intrinsic viscosity ( $\eta$ ) of 0.73 dl/g as determined in decalin at 135 °C in a weight proportion of 23/77.

【 0097 】

(3) Production of the laminate

There were blended 100 parts by weight of the ethylenic thermoplastic elastomer (A-1) of the above (1) and 3.0 parts by weight of a mixture (B-1) composed of 50 mole % of citric acid and 50 mole % of sodium hydrogen-carbonate on a tumbler type Bravender to prepare a foamable composition. This foamable composition was extrusion-molded at a die temperature of 150 °C to effect a foaming molding to form a core plate and substrate layer portions, while at the same time the ultrahigh molecular weight polyethylene composition (Y-1) of the above (2) was co-extruded to form a skin layer, whereupon the substrate layer and the skin layer were heat-fused to thereby produce a weather strip as shown in Fig. 1. The foaming expansion ratio of the resulting weather strip was 4.8 times the original

composition volume.

【 0098 】

The so-produced weather strip was assembled on a window frame for testing, whereupon a window glass having a thickness of 3.2 mm was inserted therein, in order to carry out a durability test (repeating test of up-and-down motion of the window glass). The weather strip had withstood 50,000 repetitions of up-and-down motion without suffering from any yielding phenomenon nor abrasion and had maintained its function as weather strip.

【 0099 】

Example 2

Using 30 parts by weight of the linear low density polyethylene as used in Example 1, 70 parts by weight of the ethylene/propylene/dicyclopentadiene copolymer rubber as used in Example 1 and 40 parts by weight of a softening agent based on mineral oil (a product of Idemitsu Kosan Co., Ltd. with trademark PW-380, a paraffinic oil), an ethylenic thermoplastic elastomer (A-2) was obtained in the same way as in Example 1.

【 0100 】

Then, using this resulting ethylenic thermoplastic elastomer (A-2), a foamable composition was prepared in the same way as in Example 1, from which a weather strip was produced together with the skin layer same as that prepared in Example 1. For this weather strip, a durability test was performed. This weather strip had withstood 50,000 repetitions of up-and-down motion and maintained its function as weather strip. The foaming

expansion ratio of this weather strip was 3.7 times the original composition volume.

【 0101】

Example 3

Using 15 parts by weight of the linear low density polyethylene as used in Example 1, 85 parts by weight of the ethylene/propylene/dicyclopentadiene copolymer rubber as used in Example 1 and 20 parts by weight of a propylene/ethylene random copolymer (PP-1) (MFR = 0.5 g/10 min., ethylene content = 4 mole %), an ethylenic thermoplastic elastomer (A-3) was prepared in the same manner as in Example 1.

【 0102】

Then, using this ethylenic thermoplastic elastomer (A-3), a foamable composition was prepared in the same way as in Example 1, from which a weather strip was produced together with the skin layer same as that prepared in Example 1. For this weather strip, a durability test was performed. This weather strip had withstood 50,000 repetitions of up-and-down motion and maintained its function as weather strip. The foaming expansion ratio of this weather strip was 3.0 times the original composition volume.

【 0103】

Example 4

Using 15 parts by weight of the linear low density polyethylene as used in Example 1, 85 parts by weight of the ethylene/propylene/dicyclopentadiene copolymer rubber as used in Example 1 and 20 parts by weight of a homopolymer of propylene (PP-2) (MFR = 1.5 g/10 min.),

an ethylenic thermoplastic elastomer (A-4) was prepared in the same manner as in Example 1.

【 0104 】

Then, using this ethylenic thermoplastic elastomer (A-4), a foamable composition was prepared as in Example 1, from which a weather strip was produced together with the skin layer same as that prepared in Example 1. For this weather strip, a durability test was performed. This weather strip had withstood 50,000 repetitions of up-and-down motion and maintained its function as weather strip. The foaming expansion ratio of this weather strip was 2.8 times the original composition volume.

【 0105 】

Example 5

Using 30 parts by weight of the linear low density polyethylene as used in Example 1, 110 parts by weight of an oil-extended ethylene/propylene/dicyclo-pentadiene copolymer rubber obtained by compounding the ethylene/propylene/dicyclopentadiene copolymer rubber as used in Example 1 with 40 parts by weight of an extender oil (a product of Idemitsu Kosan Co., Ltd. with trademark PW-380, a paraffinic oil), an ethylenic thermoplastic elastomer (A-5) was obtained in the same way as in Example 1.

【 0106 】

Then, using this ethylenic thermoplastic elastomer (A-5), a foamable composition was prepared in the same way as in Example 1, from which a weather strip was produced together with the skin layer same as that

prepared in Example 1. For this weather strip, a durability test was performed. This weather strip had withstood 50,000 repetitions of up-and-down motion and maintained its function as weather strip. The foaming expansion ratio of this weather strip was 3.8 times the original composition volume.

【 0107】

#### Example 6

##### (1) Production of an olefinic thermoplastic elastomer (C-1)

There were kneaded on a Bumbury's mixer 60 parts by weight of an ethylene/propylene/5-ethylidene-2-norbornene copolymer rubber (ethylene content = 70 mole %, iodine value = 12, Mooney viscosity  $ML_{1+4}(100\text{ }^{\circ}\text{C}) = 120$ ) and 40 parts by weight of a polypropylene {MFR (ASTM D-1238-65T,  $230\text{ }^{\circ}\text{C}$ , 2.16 kg load) = 13 g/10 min., density =  $0.91\text{ g/cm}^3$ } at  $180\text{ }^{\circ}\text{C}$  under a nitrogen atmosphere for 5 minutes. Then, this kneaded blend was passed through rolls into a sheet and this sheet was cut by a sheet cutter into dice-formed pellets. Then, this pelletized product was blended with 0.2 part by weight of 1,3-bis(tert-butylperoxyisopropyl)benzene and 0.2 part by weight of divinylbenzene on a Henschel mixer. Thereafter, the resulting blend was extruded by a double shaft extruder having an L/D of 40 and a screw diameter of 50 mm at  $200\text{ }^{\circ}\text{C}$  under a nitrogen atmosphere to obtain an olefinic thermoplastic elastomer (C-1). The resulting olefinic thermoplastic elastomer (C-1) had an gel content of 78 % by weight as determined by the

method given above.

【 0108 】

(2) Production of the laminate

There were kneaded 100 parts by weight of the olefinic thermoplastic elastomer (C-1) of the above (1) and 2 parts by weight of a silicone oil (D-1) (a product of Toray-Dow Corning K.K. with trademark SH200-3000 cSt) on a double shaft extruder to obtain an olefinic thermoplastic elastomer composition (Z-1) for the skin layer.

This olefinic thermoplastic elastomer composition (Z-1) was co-extruded together with the foamable composition same as that in Example 1 to produce a weather strip, for which a durability test was carried out. This weather strip had withstood the 50,000 repetition test and maintained its function as weather strip.

【 0109 】

Example 7

There were kneaded on a double shaft extruder 100 parts by weight of the olefinic thermoplastic elastomer (C-1) obtained in Example 6, 2 parts by weight of the silicone oil (D-1) used in Example 6 and 14 parts by weight of a masterbatch of silicone oil/polypropylene (D-2) {a product of Toray-Dow Coening K.K. with trademark BY27-002 (content of the ultrahigh molecular weight silicone oil = 50 % by weight)} to obtain an olefinic thermoplastic elastomer composition (Z-2) for the skin layer.

This olefinic thermoplastic elastomer composition (Z-2) was co-extruded together with the foamable

composition same as that in Example 1 to produce a weather strip, for which a durability test was carried out. This weather strip had withstood the 50,000 repetition test and maintained its function as weather strip.

【 0110 】

Example 8

There were kneaded on a double shaft extruder 100 parts by weight of the olefinic thermoplastic elastomer (C-1) obtained in Example 6 and 3 parts by weight of a fluorine-containing polymer (E-1) {a product of Sumitomo Three M K.K. with trademark DYNAMER FX-9613 (with a content of the fluorine-containing polymer of 90 %)} to obtain an olefinic thermoplastic elastomer composition (Z-3) for the skin layer.

This olefinic thermoplastic elastomer composition (Z-3) was co-extruded together with the foamable composition same as that in Example 1 to produce a weather strip, for which a durability test was carried out. This weather strip had withstood the 50,000 repetition test and maintained its function as weather strip.

【 0111 】

Example 9

There were kneaded on a double shaft extruder 100 parts by weight of the olefinic thermoplastic elastomer (C-1) obtained in Example 6 and 3 parts by weight of an antistatic agent (F-1) (a product of Kao Corporation with trademark ELECTROSTRIPPER TS-6B) to obtain an olefinic thermoplastic elastomer composition (Z-4) for the skin layer.

This olefinic thermoplastic elastomer composition

(Z-4) was co-extruded together with the foamable composition same as that in Example 1 to produce a weather strip, for which a durability test was carried out. This weather strip had withstood the 50,000 repetition test and maintained its function as weather strip.

【 0112 】

Example 10

There were kneaded on a double shaft extruder 100 parts by weight of the olefinic thermoplastic elastomer (C-1) obtained in Example 6 and 10 parts by weight of the ultrahigh molecular weight polyolefin composition (Y-1) used in Example 1 to obtain an olefinic thermoplastic elastomer composition (Z-5) for the skin layer.

This olefinic thermoplastic elastomer composition (Z-5) was co-extruded together with the foamable composition same as that in Example 1 to produce a weather strip, for which a durability test was carried out. This weather strip had withstood the 50,000 repetition test and maintained its function as weather strip.

【 0113 】

Example 11

There were kneaded on a double shaft extruder 100 parts by weight of the olefinic thermoplastic elastomer (C-1) obtained in Example 6, 100 parts by weight of the ultrahigh molecular weight polyolefin composition (Y-1) used in Example 1 and 2 parts by weight of the silicone oil (D-1) to obtain an olefinic thermoplastic elastomer composition (Z-6) for the skin layer.

This olefinic thermoplastic elastomer composition



(Z-6) was co-extruded together with the foamable composition same as that in Example 1 to produce a weather strip, for which a durability test was carried out. This weather strip had withstood the 50,000 repetition test and maintained its function as weather strip.

【 0114 】

Example 12

There were kneaded on a double shaft extruder 100 parts by weight of the olefinic thermoplastic elastomer (C-1) obtained in Example 6, 2 parts by weight of the silicone oil (D-1) used in Example 1 and 30 parts by weight of a polypropylene (G-1) {MFR (ASTM D-1238-65T, 230 °C , 2.16 kg load) = 13 g/10 min., density = 0.91 g/cm<sup>3</sup>)} to obtain an olefinic thermoplastic elastomer composition (Z-7) for the skin layer.

This olefinic thermoplastic elastomer composition (Z-7) was co-extruded together with the foamable composition same as that in Example 1 to produce a weather strip, for which a durability test was carried out. This weather strip had withstood the 50,000 repetition test and maintained its function as weather strip.

【 0115 】

Comparative Example 1

Using a conventional weather strip (having a laminate structure in which a nylon film is fitted on a layer of a soft vinyl chloride resin layer), the durability test was carried out in the same way. In this test, a breakdown occurred on the face contacting with the window glass after 25,000 repetitions, whereby the friction resistance

on the window glass increased considerably to thereby render practical use impossible.

【 0116】

The conditions of the dynamic heat treatment in the production of the ethylenic thermoplastic elastomers (A-1), (A-2), (A-3), (A-4) and (A-5) are given in Table 1 below.

【 0117】

【 TABLE 1 】

Table 1

Elastomers		A-1	A-2	A-3	A-4	A-5
<u>Composition</u>						
PE	*1	30	30	15	15	30
EPDM	*2	70	70	85	85	-
O-ext. EPDM	*3	-	-	-	-	110
PP-1	*4	-	-	20	-	-
PP-2	*5	-	-	-	20	-
Paraff. oil	*6	-	40	-	-	-
<u>Prod. conditn.</u>						
T	*7	223	222	239	238	225
P	*8	50	50	50	50	50
Q	*9	2800	2800	2800	2800	2800
R	*10	50	50	50	50	50
S	*11	280	280	280	280	280
U	*12	15.7	15.7	15.7	15.7	15.7
Value of formula (1)	*13	6.42	6.41	6.58	6.57	6.44

【 0118 】

Notes: Numbers given in the column of composition are those based on weight parts.

\*1 : PE denotes linear low density polyethylene.

\*2 : EPDM represents ethylene/propylene/dicyclo-pentadiene copolymer rubber.

\*3 : O-ext. EPDM denoted an oil-extended ethylene/propylene/dicyclopentadiene copolymer composed of 100 parts by weight of ethylene/propylene/dicyclopentadiene copolymer rubber

blended with 40 parts by weight of a paraffinic extender oil (a product of Idemitsu Kosan Co., Ltd. with trademark PW-380).

\*4 : pp-1 represents a propylene/ethylene copolymer.

\*5 : pp-2 represents a homopolymer of propylene.

\*6 : Paraff. oil represents a softening agent based on mineral oil (a product of Idemitsu Kosan Co., Ltd. with trademark PW-380).

\*7 : T represents the resin temperature at the die outlet.

\*8 : P represents the screw diameter in mm of the double shaft extruder.

\*9 : Q represents the maximum shearing velocity in  $\text{sec}^{-1}$  imposed in the double shaft extruder.

\*10: R represents the extrusion throughput in kg/hr of the double shaft extruder.

\*11: S represents the revolution frequency per second in rps.

\*12: U represents the distance in mm of the clearance between the barrel inner face and the kneading segment of the screw at the narrowest portion thereof.

\*13: The value calculated by the formula

$$[\{(T-130)/100\} + 2.2 \cdot \log P + \log Q + \log R] \quad (1)$$

## 【 BRIEF DESCRIPTION OF THE DRAWINGS 】

### 【 FIG. 1 】

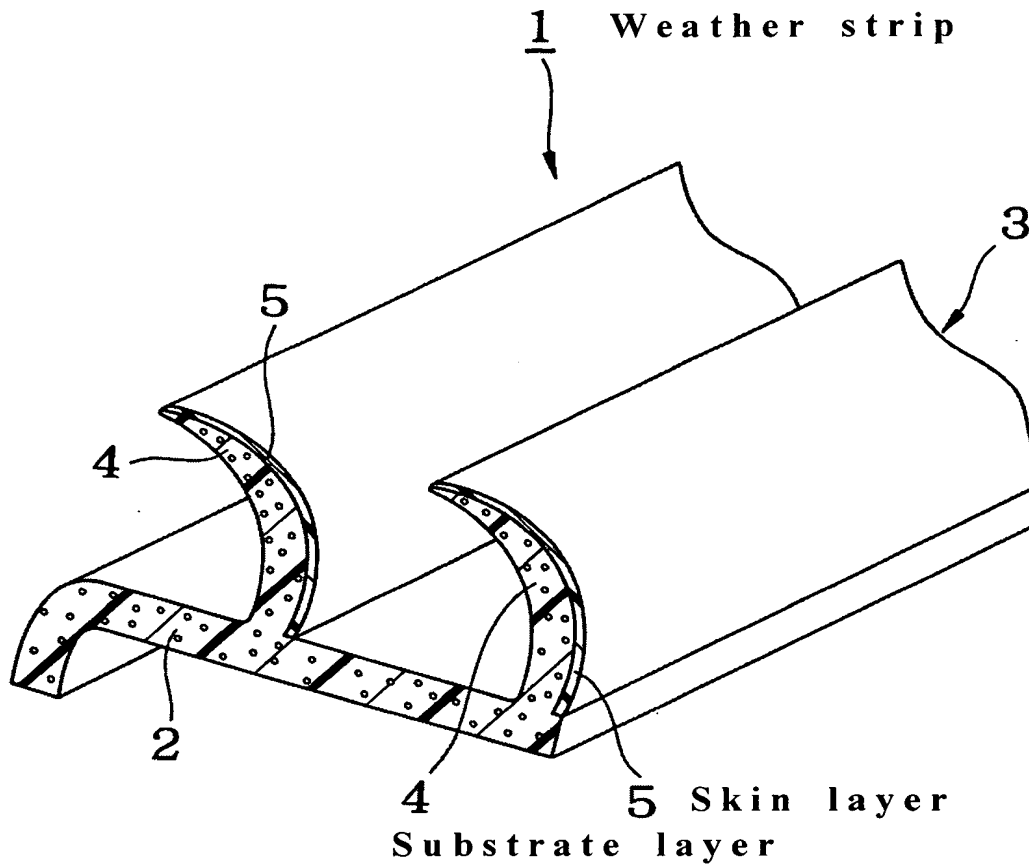
Fig. 1 shows a weather strip comprising the foamed laminate based on olefin according to the present invention in a perspective view, in which a cross section

is shown by the front face.

**【 EXPLANATION OF SYMBOLS 】**

- 1 .... Weather strip
- 2 .... Core plate
- 3 .... Contact seal lug
- 4 .... Substrate layer
- 5 .... Skin layer

【 DESIGNATION OF THE DOCUMENT 】      DRAWINGS  
【 FIG. 1 】



【 DESIGNATION OF THE DOCUMENT】      ABSTRACT  
OF THE DISCLOSURE

【 ABSTRACT】

【 PURPOSE】

We provide a foamed laminate based on olefin which is made of an olefinic polymer premitting recycled use and obtainable at a high foaming expansion ratio and, thus, exhibits a soft hand touch and which is superior in the appearance, in the resistance to abrasion, in the durability and in the sliding performance.

【 CONSTRUCTION】

A foamed laminate based on olefin in which  
a substrate layer, consisting of a foamed body of a ethylenic thermoplastic elastomer composition comprising the ethylenic thermoplastic elastomer and the foaming agent to foaming comprising a polyethylene resin and a copolymer based on ethylene/ $\alpha$ -olefin which has a Mooney viscosity  $ML_{1+4}(100\text{ }^{\circ}\text{C})$  of 90 - 250 and an ethylene content of 70 - 95 mole %, and

a skin layer made of an ultrahigh molecular weight polyolefin resin (Y) which has an intrinsic viscosity ( $\eta$ ) of 3.5 - 8.3 dl/g or an olefinic thermoplastic elastomer composition which comprises an olefinic thermoplastic elastomer, at least one kind selected from the group consisting of an organopolysiloxane, a fluorine-containing polymer, an antistatic agent, and a polyolefin resin,

are laminated.

【 SELECTED DRAWING】      NONE

INFORMATIONS ON HISTORY OF THE APPLICANT

Identification Number [000005887]

1. Date of Revision 1st October 1997

[Reason of Revision] Change of Name

Address 2-5, Kasumigaseki 3-Chome, Chiyoda-Ku  
Tokyo, Japan

Name MITSUI CHEMICALS, INC.